

## CHAPTER 1

### INTRODUCTION

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#### 1.1. History

The first reports of the deposits known today as plasma polymers appeared in the second half of the 19<sup>th</sup> century [1, 2]. Several papers treating these films and related to plasma polymerization processes were published in the 1930s [3-6] and more attention was paid to the subject in the 1950s [9-10]. König and Helwig [7] deliberately deposited films that would be described nowadays as hydrocarbon plasma polymers. Basically, they used a glass bell-jar with parallel plate electrodes (made of Al) that were powered by singly rectified 50 Hz voltage up to 2 kV. Their “pulsing” DC glow discharge was operated in benzene vapours and films were deposited on various substrates resting on the anode. Films up to 1  $\mu\text{m}$  thick on glass were yellowish in transmitted light and their density was about 1.4  $\text{g}/\text{cm}^3$  and electrical conductivity was  $10^{-9} \Omega^{-1} \text{cm}^{-1}$ . After annealing these films started to change at 100  $^{\circ}\text{C}$  and at 400  $^{\circ}\text{C}$  turned fully into carbonaceous films. The use of these films for carbon foils was proposed. Brokes and König [8] deposited films not only from benzene but also from methane and presented their absorption IR spectra. The absorption IR spectra, and the absorption in the visible region of light of plasma polymerized benzene films deposited at the increased voltage 500 V, 800 V and 3000 V, showed the transition from a hydrocarbon plasma polymer to a hard plasma polymer (now mostly denoted as C:H) as a consequence of the increased energetic ion bombardment. A more detailed study of the deposition process was published by Heisen [9]. Energetic particles from the discharge (positive ions and electrons) bombard the adsorbed benzene molecules on the substrate surface. Originated fragments react with the other molecules and a plasma polymer film grows. The above described early period of the plasma polymer field has been

nicely reviewed by Pagnia [11].

In the 1960s, especially during the early development of the microelectronics research and industry, rapid growth of plasma polymerization started that was inspired by the hope to use a plasma polymer as a dielectric film [12]. Bradley and Hammes [13], who continued previous work [12], plasma polymerized up to 40 monomers in a parallel plate electrode bell jar arrangement using AC voltage at 10 – 50 kHz frequency. These monomers included acetylene, styrene, naphthalene, etc. and certain metalorganics, such as ferrocene, diphenyl mercury etc. The authors measured the electrical properties of the prepared films that were sandwiched between Al electrodes. The intensive attempts to develop the new dielectric film were continued by Stuart [14,15], Bashara and Doty [16], Williams and Hayes [17], Gregor [18] and Hirai and Nakada [19]. The two reviews [20, 21] appeared that discussed glow-discharge (plasma) polymerization, however, they also considered polymer films deposition techniques such as electron bombardment of organic vapors or their exposure to UV light. Another proposed technique was simple vacuum evaporation [22-23]. When heated to the evaporation temperature, most polymers fragment. The gaseous fragments then condense on the substrate without creating a polymer network. Without additional e.g. UV light irradiation this deposition technique is applicable only in special cases (low molecular weight polymers). This subject was reviewed in detail by Hogarth and Igbal [24]. In recent years the ionization-assisted method (IAD) was developed [25]. Species evaporated from the evaporation source are ionized by the electron shower (across the beam of evaporated particles) and are accelerated towards the substrate. The ion concentration is typically from 0.1 to 1 % of the depositing material and ion energy around several hundred of eV.

Once the plasma polymerization process was recognized, it started to be investigated because of many potential applications. These included, not only electrical but also, optical field, various surface modifications especially for biomedical applications, etc. The number of published studies has increased, and several reviews [26-36] and monographs appeared [37-41].

## 1.2. What is a Plasma Polymer?

The term plasma polymer denotes a material that is created as a result of a passage of an organic gas or vapor through the glow discharge - more generally one should say an electric discharge in an organic gas. Usually, it is deposited in

the form of a thin film. In spite of the use of the word polymer, the plasma polymer means a new class of material that has only a little in common with the conventional polymer that has regularly repeating units (please see Fig.1.1). In the case of the plasma polymer, the chains are short and in addition they are randomly branched and terminated with a high degree of crosslinking (please see Fig.1.2). In most cases, a great number of free radicals are trapped within the network. These radicals cannot recombine rapidly and therefore when the plasma polymer is exposed to the open atmosphere they react with the oxygen and water vapor. These free radicals are the cause of often observed aging processes in plasma polymers. Plasma polymers possess a rather disordered structure and this depends on the intensity and energy of the species bombarding the growing film.

The plasma polymerization process involves reactions between plasma species, between plasma and surface species, and between surface species [31]. Usually a free radical mechanism is considered and the two cases are distinguished: 1) plasma-state polymerization and 2) plasma induced polymerization.

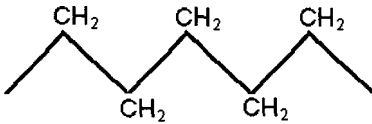


Figure 1.1 HDPE

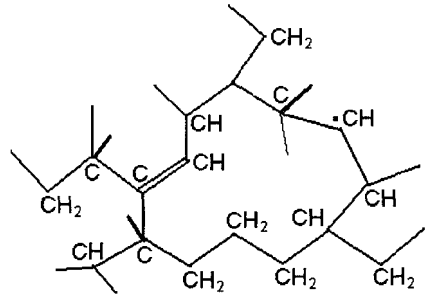


Figure 1.2 Hypothetical structure of a hydrocarbon plasma polymer

Plasma-state polymerization occurs only in a plasma of an electric discharge in the presence of organic molecules. Energetic particles but mainly energetic electrons produce, in the collisions with organic molecules, a number of species (fragments) i.e. also free radicals. These undergo chain reactions and free radical termination reactions. As a result, any organic compound in the gaseous state may be plasma polymerized.

Plasma induced polymerization is essentially free radical induced polymerization of molecules including unsaturated carbon-carbon bonds. In

most cases, the term of plasma polymer is used in the case of plasma-state polymerization.

The terms plasma polymerization and plasma polymer originated historically and are commonly accepted. However, some researchers suggest that it is more accurate to use the terms PECVD (plasma enhanced chemical vapor deposition) of organic compounds and plasma deposited coatings, respectively. If one has in mind the definitions of these terms any of them are correct to apply. Throughout this book mostly the former ones are used.

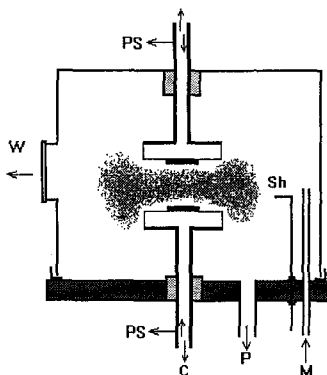
### 1.3. Deposition Systems for Plasma Polymerization

The plasma polymerization process is carried on usually in a low pressure, low temperature plasma. An atmospheric plasma is becoming more and more popular for deposition including plasma polymers. This topic will be specially treated in Chapter 8.

A great number of deposition systems using low pressure plasma was described in the literature and summarized in Refs 26-41. Generally, the three classes of plasma polymerization deposition systems (reactors) can be distinguished, as pointed out by Shi [33]: (a) internal electrode reactors, (b) external electrode reactors, and (c) electrodeless microwave or high frequency reactors.

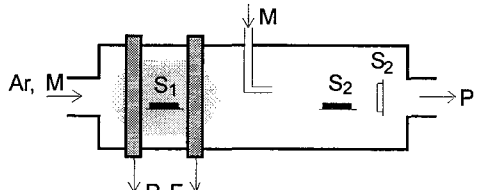
The leading configuration in the group (a) is a bell-jar-type reactor with internal parallel plate electrode arrangement (Fig.1.3). The discharge can be excited either by DC or AC and/or RF voltage. DC is used in special cases or in the case when a planar magnetron is used (please see Chapter 9). The magnetron electrode serves as a cathode and is at high negative potential (several hundred volts) while the counterelectrode serves as an anode and is usually connected to the stainless steel-bell-jar and earthed (asymmetrical arrangement). The "anode" (substrate holder) may be also isolated and in this case biased.

For a plasma polymerization process, more typical is the discharge excitation by



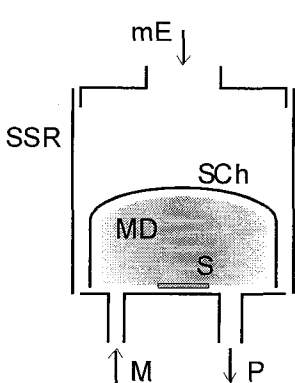
**Figure 1.3.** Deposition systems: (a) parallel plate (internal) electrode reactor (PS - to power supply, C - cooling, W - window, P - to pumps, M - monomer, Sh - shutter, S - substrate)

AC and RF voltages in so called symmetrical arrangement. If the frequency of the excitation voltage is above about 50 kHz (100 kHz), the power must be delivered through a matching unit and determined by a power meter. In the case of the asymmetrical arrangement where the excitation electrode is connected to the power supply through a blocking capacitor and matching unit, a DC negative bias is developed on this electrode. In this case, the surface (target) of the excitation electrode is sputtered by positive ions (RF sputtering). In some processes this may be the reason for concern as there is a danger of impurities sputtered off from the excitation electrode. In other cases this may be welcome e.g. simultaneous plasma polymerization and co-sputtering of the metallic target for composite metal/plasma polymer film deposition (please see Chapter 9).



**Figure 1.4.** Tubular glass or silica deposition system  
Ar-argon, M - monomer, S<sub>1</sub>, S<sub>2</sub> - substrates, P - pumps)

External electrode reactors use ring electrodes (Fig.1.4) or an external coil around a tube from glass or silica. Rf power may be coupled into the plasma inductively but in most cases the coupling is of a capacitive nature [42]. Therefore when the external coil is used instead of the term inductive coupling one could use inductive excitation to point out the use of the coil but to avoid the confusion as the coupling is likely capacitive. This reactor then cannot be



**Figure 1.5.** A type of a microwave reactor (mE - microwave energy, MD - microwave discharge, SSR - stainless steel resonator, Sch - silica chamber, S - substrate, M - monomer, P - to pumps)

considered as electrodeless as the DC negative bias appears on the inner reactor wall under the coil turn or under the ring electrode (please see the discussion in Ref. 41) The substrate is positioned inside the plasma or downstream of the plasma. Electrodeless microwave reactors are usually composed from a silica tube that passes through the resonant cavity coupled to a microwave power supply (typically 2.45 GHz).

Plasma is generated in the tube within the cavity and substrates are positioned downstream of the plasma. The cavity actually acts instead of the RF excitation coil or ring electrodes in Fig.1.4. In Fig.1.5 another type of microwave reactor is shown that resembles a "microwave oven" of more

sophisticated resonator type shape (not shown in schematic). Some other types of microwave reactors were designed – please see Refs. 41 and 43.

#### 1.4. Deposition (Plasma) Process Parameters

The structure and composition, physical and chemical properties of a plasma polymer and its deposition rate depend on many parameters for a given monomer (feed gas) or gas mixtures:

- (a) The type of the reactor and its geometrical configuration
- (b) Frequency of the discharge excitation voltage (for RF continuous wave mode or pulsing mode)
- (c) Power delivered to the discharge ( $0.001 - 2.5 \text{ W/cm}^3$ )
- (d) Flow rate of the monomer ( $1 - 100 \text{ cm}^3 \text{ (STP)/min}$ )
- (e) Working gas pressure ( $1 - 100 \text{ Pa}$ )
- (f) Substrate temperature
- (g) Substrate size and its position

If the type of reactor and frequency of the excitation voltage are chosen, substrate position and size are fixed, then one should optimize the deposition rate in dependence on power, flow rate and working gas pressure. Usually, one of these parameters is changing while the other two are kept constant. In this case we find that the deposition rate increases with power until all available monomer at a concentration given by working pressure and supplied at the constant flow rate is consumed. Further increase of power has no effect and the deposition rate is constant. Resulting deposition rate is given by the growth rate and competing ablation rate for some fluoro(chloro)carbons and hydrocarbons containing oxygen, the deposition rate may decrease for higher powers as the ablation start to dominate.

Similar deposition rate curve is obtained when pressure is the variable. When pressure and power are kept constant and the flow rate is increased – the deposition rate also increases. When the flow becomes too high at a given power level not all supplied monomer can be excited. Some of the excited species are even drawn away from the substrate and cannot take part in the deposition. The deposition dependence on the flow rate has a maximum.

As may be seen, for proper optimization of the deposition rate, very large amount of measurements are needed. This can be speeded up by a “process analysis“. Also homogenous thickness deposition should be optimized in respect to the substrate size.

The substrate temperature is important. With decreasing temperature the deposition rate of a plasma polymer increases. This is because plasma polymer deposition carried out at decreased pressure is governed by the adsorption processes. However, not only the deposition rate but the structure of the plasma polymer changes. For certain monomers used at decreased substrate temperature, the plasma polymer retains more of the molecular structure of the monomers. But physical structure may also change giving rise to so called columnar structure – please see Chapter 9.

Our last remark is to the frequency of the excitation voltage. As mentioned before, DC voltage is rarely used. If AC voltage is applied with a frequency less than 100 Hz, it is basically of DC type with changing polarity, but it switches off between half cycles. If the frequency is further increased up to the point and above when the time needed for positive ions to move, from the momentary anode to cathode becomes equal to 1/2 of the period of the voltage, not all positive ions originating at anode can transit to the cathode before the voltage is reversed. This causes partial retention of the positive space charge from one half cycle to the next and helps reinitiation of the discharge. Because of the low mobility, the positive ions are unable to move during each half cycle while the electrons are swept through the interelectrode space by the voltage on each half cycle. As a result, a pulsating negative sheath voltage on the walls (electrodes covered by a dielectric film) appears. We are in the range of RF discharge. DC negative bias will appear on the surface (electrode) covered by a dielectric or connected to RF power supply through the blocking capacitor. Generation of positive ion – electron pairs takes place in the plasma volume and does not depend on the processes on the electrodes. In contrast, DC type discharges are dependent strongly on the processes at the cathode where the electrons are emitted by bombarding positive ions. After the acceleration through the dark cathode space, the electrons, in ionization collisions with the neutral gas, create pairs electron-positive ion that is necessary for sustaining the DC discharge. In a microwave discharge, the transfer of power to the plasma particles and especially electrons is much more efficient than in RF discharge and as a result, more electrons with higher energies are present. Deposition rate is increased as a result of increased efficiency of the plasma polymerization process in this case. For more details, please, see Refs. 27, 28, 33, 41.

In order to be able to transfer the deposition process to another apparatus or to perform the scale-up, the detailed description of plasma-chemical processes is needed. This is done by means of *in situ* diagnostics such as OES (optical emission spectroscopy), IR (infrared) absorption spectroscopy of the plasma,

MS (mass spectroscopy) or corpuscular diagnostics and LP (Langmuir probes). Because of their importance, the first three methods will be discussed in detail in the Chapters 2, 3 and 4, respectively.

### **1.5. Models of Plasma Polymerization**

Williams and Hayes [17] excited an AC (10 kHz) discharge in styrene at a pressure 0.1 – 3 torr using a bell-jar-type reactor with a parallel plate electrode system. They found, that at constant substrate temperature and constant flow of styrene, the polymerization rate at first increased and then reached saturation with either increased pressure at constant discharge current or with increased current at a constant pressure. They also found that the polymerization rate increases with decreasing substrate temperature. Plasma polymer formation proceeds as follows. Positive ions are formed by collisions between the energetic electrons and monomer molecules in the negative glow. These ions are attracted to the electrodes and bombard in the first stage of growth adsorbed monomer molecules. These are activated (fragmented) and react with the unactivated monomer molecules. When the first layers of plasma polymer are created not only adsorbed monomer molecules are activated but also polymer surface molecules. These active species propagate the polymerization reaction by addition of unactivated molecules.

Denaro et al. [46-48] proposed the explanation of plasma polymerization of styrene (at 1 torr) and some other monomers in a 2 MHz discharge. The initiation of the polymerization reaction was done by energetic electrons bombarding the polymer film that was covering the electrodes and resulted in the creation of surface free radicals that react with the adsorbed monomer molecules. They obtained a good agreement with the experiment in case of allyl alcohol [48]. A similar model was proposed by Westwood [49] who used a parallel-plate electrode system in RF discharge and relied in his model on activation by bombarding positive ions.

Poll et al. [50,51] developed a detailed model based mainly on the processes on the surfaces adjacent to the discharge region, e.g. adsorption, desorption and polymerization. He also considered processes leading to the formation of new compounds by the transformation of the monomer under the influence of the discharge (for more details see also Ref. 41). Comparison to the experiment is done for  $C_2F_4$ .

Lam et al. [52] developed a model of plasma polymerization of styrene in a RF (800 kHz) discharge using a capacitively coupled parallel plate electrode system. Three steps were considered: (1) Initiations of monomers by electron impact was followed by (2) propagation and (3) termination as in conventional polymerization. Free radical polymerization was assumed. Four mechanism models were examined considering the above mentioned three steps taking place either in the gas phase or on the surface. Comparing the theory and experiment, the following model seemed to be the most probable: Monomers are activated in the gas phase via collisions with energetic electrons. They diffuse to the surface where they react in propagation reactions with adsorbed monomers and subsequently terminate.

A similar model as above for plasma polymerization of unsaturated hydrocarbons in a RF discharge was proposed by Tibbitt et al. [52].

The overall scheme of plasma polymerization based on Poll's et al. [51] work was proposed by Yasuda and Hsu [52] that involves the competitive ablation and polymerization mechanism (CAP). A monomer passing through the plasma zone is turned into the complex mixture of untact monomer, its excited or ionized fragments and gaseous products that do not participate in plasma polymerization. Yasuda suggests that plasma polymerization can be explained by a bicyclic step-growth mechanism. The first cycle relies on monofunctional species while the second one on bifunctional species. For more details, please, see Refs. 29 and 41.

## 1.6. Types of Plasma Polymers and their Characterization

According to the type of monomer used several types of plasma polymers are distinguished [30, 33]: hydrocarbon, fluoro(chloro)carbon nitrogen containing plasma polymers and composites.

A number of characterization techniques are used that include: FTIR, XPS, AES, SIMS, RHEED, NMR, ESR, ERDA, RBS, NRA, DSC, TGA, XRD(SAXS), SEM, AFM (STM). Most frequently used are FTIR, XPS, RBS, ERDA, SEM, AFM.

Electrical properties are studied by conventional DC techniques, AC properties by dielectric spectroscopy.

Optical properties in the visible region use transmission and absorption and ellipsometric measurements.

Surface properties such as wettability (contact angle) [41], adhesion (Scotch tape test or various scratch testers), and mechanical properties such as internal stress, hardness, abrasion and friction are measured by routine thin film methods (for more details see [53]).

## 1.7. Conclusions

A number of applications were proposed, some of them mainly as protective and optical films and layers for packaging and in the biomedical field. The applications are summarized in several reviews and monographs e.g. [29,31,33, 34,35,39,41]. However, some features of plasma polymers should be improved such as suppression of ageing etc. for their wider applications. Therefore, further investigations are needed in order to employ all potentially attractive properties of plasma polymers. In the following chapters, the reader will find the state of the art of the field and its current developments.

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